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GAS-PHASE OXIDATION OF ALUMINUM ATOMS

Richard N. Zare

Columbia University

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Prof. Richard N. Zare
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A. Summary

During the course of this grant we have accomplished the following tasks:

1) We have studied the chemiluminescent reaction $Al + O_3 \rightarrow AlO* + O_2$ and based on an analysis of the observed AlO $B^2\Sigma - X^2\Sigma$ blue green band system we have placed a lower bound on $D_0^0 (AlO)$ of 5.13 ± 0.05 eV and have suggested that the actual value of $D_0^0 (AlO)$ will be only at most a few tenths of an eV higher.

2) We have developed a new technique for detecting reaction products using laser-induced fluorescence and we have applied this technique to study the ground state BaO molecules formed in the reaction

$$Ba + O_2 \rightarrow BaO + O$$

for which we have deduced an approximate vibrational temperature for the newly formed BaO products.

3) We have designed, constructed, assembled, and tested a new metal oven capable of producing beams of aluminum atoms so that the reaction

$$Al + O_2 \rightarrow AlO + O$$

can be studied under single-collision conditions using laser-induced fluorescence as an AlO detector.

B.   Chemiluminescent reactions involving aluminum

In a molecular beam apparatus, a thermal beam of aluminum atoms ($\approx 1700^\circ$K) traverses a scattering chamber containing ozone molecules (300°K), and the resultant visible chemiluminescence is recorded with a 1m scanning monochromator. The chemiluminescence spectrum consists of (a) the AlO $B^2\Sigma^+ - X^2\Sigma^+$ blue-green band system for which we have assigned bands to the strongly structured features in the 4200-4900Å spectral region, and (b) a more intense but weakly structured continuum in the region 4500-8500Å which appears to be emission from a polyatomic aluminum oxide, most likely, AlO_2. By identifying that up to the $v'=17$ level of the B state is populated in this reaction, we are able to place a minimum value of 5.13 $\pm$ 0.05 eV on the AlO bond energy i.e. the dissociation energy of the AlO ground state molecule. By accepting the upper limit of 5.20 eV deduced by MacDonald and Innes[1] from Tyte's[2] shock tube absorption data, we recommend the value D_0^0(AlO) = 5.15 $\pm$ 0.05 eV. This work has been published in the Journal of Chemical Physics.[3]

C.   Laser-Induced fluorescence as a molecular beam detector

Traditionally, molecular beam kinetic studies have relied on surface ionizers or electron-impact-ionizer-massfilters to detect the reaction products. However, both these techniques

are "blind" to the internal state of excitation of the products.
We have developed a new technique that overcomes this blindness
by using light in the detection scheme. Here, a tunable dye
laser is scanned in wavelength and the fluorescence of the
reaction products are detected. Whenever the wavelength of the
laser beam coincides with a molecular absorption line, cor-
responding to a specific $(v,J) \rightarrow (v',J')$ transition, those mole-
cules in the (v,J) are excited and subsequently fluoresce. By
measuring the intensity of the fluorescence signal as a function
of laser wavelength, it is possible to deduce the relative
(v,J) population distribution from a knowledge of Franck-Condon
factors and photomultiplier wavelength response factors.

The first successful demonstration of this new molecular
beam detector was the observation and analysis of the BaO
ground state (v,J) distribution resulting from the reaction
$Ba + O_2 \rightarrow BaO + O$. This work has been reported in the Journal
of Chemical Physics.[4] Here it was shown that it was possible
to resolve the rotational structure of the BaO bands in a
slow scan using a not very narrow $(0.5Å)$ laser bandwidth.
The vibrational distribution was found to fit moderately well
a Boltzmann distribution of $2500°K$, but the rotational distribution
seemed much cooler. Subsequent work (not published) has shown
that the rotational distribution was collisionally relaxed at
the high pressures used in the slow scan and that the
rotational distribution is much hotter, approximately

comparable to the vibrational temperature. The BaO A state

lifetime was also measured. Using a swept narrow sampling

window, our first lifetime measurements give a value of

350 ± 50 nsec, in reasonable agreement with Johnson.[5]

D. Unfinished Work and Future Plans

During the second half of this grant period, a major

effort has been placed on generating in a reliable and controllable

manner aluminum beams of useful fluxes. We have succeeded in

accomplishing this by using a boron nitride crucible placed inside

a resistance-heated tantalum tube surrounded by tantalum heat

shields. This oven is very similar in design to that of Dagdigian,

and Wharton.[6] Various crucible materials were tried. Carbon proved

to be porous; molybdenum and tantalum form amalgrams. The chalky

boron nitride container occasionally fractures but is not

chemically attacked at the operating temperature of about

$1350°C$. The boron nitirde crucible normally lasts about 10

hours. A tapered stopper is used in order that the oven can

be refileed between runs.

In addition, a new vacuum chamber has been fabricated for

the forthcoming $Al + O_2$ reaction studies. This chamber has

been designed with removable sides to enable easy access to the

Al oven and to provide flexibility in the design of future

experiments. The chamber is pumped by a 6" diffusion pump.
This results in over a factor of ten increase in the differential
pumping between the oven chamber and the reaction chamber over
that previously obtained. Strong differential pumping ensures
that the reaction does not occur within the oven chamber, such
as on hot metal surfaces.

The immediate future plans are to investigate the reaction
$Al + O_2 \rightarrow AlO + O$. Attention will be directed to 1) the highest
v" level populated in the reaction (from which a new estimate of
the AlO ground state dissociation energy can be obtained),
2) the vibrational-rotational distribution (which bears on
the infrared emission from the species) and 3) the AlO $B^2\Sigma^+$
state radiative lifetime (which also bears on the importance of
AlO as an infrared emitter).

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